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13. ABSTRACT (Maximum 200 words)

Our study of LT GaAs in the previous contract is furthered by: (i) employing several novel techniques to investigate the defects present and the transport mechanism in LT GaAs, (ii) expanding to other LT-III/V compounds, and (iii) exploring the unique properties of these LT-semiconductors for device applications. Photocurrent spectroscopy of annealed LT GaAs gives clear evidence of substantial presence of As_{Ga} defects in the material. The "internal photoemission" spectrum is actually found to be due to photoexcitation from As_{Ga} defects. Magnetic circular dichroism and near-infrared absorption provide sensitive and quantitative measurements of the concentration of the As_{Ga} defects in both neutral and positively charged states. A systematical study of materials grown and annealed at different temperatures shows that As_{Ga} defects can account for the pinning of Fermi energy and play a dominant role in the materials. Nuclear magnetic resonance has started to be used to study LT GaAs. Although the study is in its early stage, it has been demonstrated that by using a spin echo technique, it is possible to obtain characteristic responses from As in perfect sites and defective sites. In contrast to LT GaAs, LT InP was found to be highly conductive. A comprehensive analysis of LT InP by a variable-temperature and high pressure Hall effect measurements, deep level transient spectroscopy, optically detected magnetic resonance (ODMR), high-resolution photoluminescence (PL) as well as ODMR- and PL-excitation spectroscopy gives direct evidence that the electronic properties of LT InP are determined by P_{In} defects. The defect provides electrons to the conduction band via auto-ionization processes. It is responsible for the n-type character of the P-rich InP. The energy positions of $P_{In}{}^{0/+}$ and $P_{In}{}^{+/++}$ have been determined for the first time to be 0.12 eV above and 0.22 eV below the conduction band, respectively.

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1. Introduction

Thin films of GaAs and related compounds grown by MBE at very low temperatures (LT GaAs) have attracted great interest in the last few years due to their unique properties [1,2]. Based on the pioneering work of Smith and Calawa at Lincoln labs [3] and early industrial evaluation at Hewlett Packard [4] they are now already used in commercial devices as buffer layers for device isolation. In the near future, applications as gate isolation layers, photoconductive switches in THz technology can be expected [5]. The unique electronic properties of this material, combining high electrical resistivity, high breakdown voltage, and ultra-short lifetime are directly related to the fact that these novel materials can be grown far off perfect stoichiometry, with up to 1.5-2% of excess anions [3, 6].

Our research of LT GaAs began in 1988 with the first contact (AFOSR-88-0162, 15 Apr 88 - 14 July 91). The effort continues in present contract (AFOSR-91-0321, 1 May 91 - 30 April 94). Within these contracts we have made several key contributions to the fundamental understanding of the electronic properties of LT GaAs, and other III/V semiconductors such as LT InP. We have also explore and compare the unique properties of these low-temperature-grown semiconductors and their potentials for device application. This includes significant progress in the analysis and understanding of a completely unexpected effect, superconductivity due to In inclusions generated during the growth of LT GaAs.

2. Summary Review of Previous Contract Accomplishments (*AFOSR-88-0162, 15 Apr 88 -14 July 91*)

The research of our first contract was concentrated on a pioneering study of LT GaAs as-grown between 190 and 300 °C, and upon in-situ and ex-situ annealing [7]. A comprehensive analysis by electron paramagnetic resonance (EPR), near-infrared absorption, Hall effect, X-ray diffraction, and particle-induced X-ray emission showed that the transport in these very As-rich layers in the as-grown state is dominated by hopping conduction between localized arsenic antisite defects present in concentrations up to 10^{20} cm^{-3} and partly compensated by up to 10^{18} cm^{-3} acceptors. The total concentration of excess As reached values of $6x10^{20}$ cm^{-3}, corresponding to [As]/[Ga]=1.03. This was found to occur together with a lattice expansion of up to 0.15%. Thermal annealing to temperatures higher than 500 °C resulted in disappearance of the lattice expansion, a reduction of the antisite defect concentration by at least two orders of magnitude, and the disappearance of hopping conduction. Optically detected magnetic resonance (ODMR) experiments using luminescence emission were successfully implemented, but the luminescence emission of LT GaAs turned out to be too small for detection by ODMR.

3. Major Accomplishments of the Present Contract (*AFOSR-91-0321, 1 May 88 - 30 Apr 94*)

Our main goal of this contract is three folds: (i) Further the understanding of the defects present and of the transport mechanism in LT GaAs, not only in as-grown, but also in annealed materials. This is fulfilled by employing several novel approaches in conjunction with the characterization techniques previously used. (ii) Expand our study to other low-temperature-grown III/V compounds, such as LT InP, investigating their fundamental similarity as well as striking difference as compared to LT GaAs. (iii) Explore and compare the unique properties of these low-temperature-grown semiconductors and their potentials for device application. This includes the study of some completely unexpected effect, such as the further analysis of superconductivity due to In inclusions generated during the growth of LT GaAs.

3.1. Low-temperature-grown GaAs

The dominant point defect in As-rich GaAs is the anion antisite defect As_{Ga}, which has been determined more than 10 years ago to be a double donor with a midgap level that is commonly called EL2 [8]. This defect dominates the electronic properties of bulk semi-insulating GaAs crystals that are grown slightly As-rich (see, e.g. [9]), so that it is straightforward to expect them to play an important role in As-rich LT GaAs thin films, too. They have indeed been identified in as-grown layers in concentrations up to 10^{20} cm^{-3}, so high that hopping conduction between these deep, localized defects makes the as-grown LT GaAs layers conductive [6,10,11]. After annealing, their concentration drops by at least two orders of magnitude [12]. However, simultaneously, As-precipitates are formed upon annealing [13,14]. This resulted in a long-standing controversy [1,2] — whether metallic As precipitates form buried Schottky barriers and thus deplete the material of carriers, as suggested by Warren et al. [15], or whether the residual As_{Ga} antisite defects dominate the electronic properties of this important material.

In order to decide the controversy around carrier transport and relaxation in *annealed* LT GaAs, two types of experiments were performed: photocurrent spectroscopy ("internal photoemission") that was regarded as the main proof of the so-called "buried Schottky barrier model" [16], and magnetic circular dichroism measurements of antisite defect concentrations.

3.1.1. Photocurrent Spectroscopy of annealed LT GaAs

Excitation of semiconductors with sub-bandgap light can result in photocurrent if defects absorb the light and emit free carriers. In the normal case of deep level defects, this is at least a two step process, with the spectral dependence dominated by the photoionization cross sections of the transitions involved. If the carriers are generated by "internal photoemission" from metallic inclusions in the crystal, the spectral dependence should be distinctly different, as now the transitions come from a band of states rather than from discrete levels. The papers by McInturf et al. [16, 17] presented results from photo-emission measurements of GaAs and AlGaAs p-i-n structures with an LT-grown highly resistive "i" layer that resulted in an almost straight Fowler plot of the square root of the photoresponse vs. photon energy for the photon energy range from 0.8 to 1.1 eV. However, such a straight Fowler plot can only be expected for the case of a planar metal/semiconductor interface, as it rests on the assumption that only carriers with enough

momentum perpendicular to the barrier can contribute to the photocurrent. For the case of small metallic clusters, all carriers excited with sufficient energy to overcome the barrier will contribute to the photocurrent, and a linear photoyield vs. energy would be expected, see the discussion in Ref. [17].

We designed a similar experiment with LT GaAs, but included low-temperature studies with a better signal-to-noise ratio and extended photon energy range [17, 18]. We performed our measurements on n^+-LT-p^+ structures at T=8 K. The LT layers were grown at 225°C and annealed, the reference sample had GaAs grown at 600°C instead of LT GaAs. The spectral dependances of the photocurrent before and after sub-band-gap light illumination are presented in Fig. 1. The reference sample showed no photocurrent upon illumination with sub-band-gap light, while the n^+-LT-p^+ structures were extremely light sensitive. All photocurrent spectral dependances show a smooth spectrum with three onsets at 0.75 eV, 1.1 eV and 1.3 eV. Superimposed on it there is a broad band centered at 1.18 eV. Upon illumination about 68% of the original photocurrent is partially quenched. It has to be mentioned that the onset energies match very well the threshold of the photoionization of the EL2 defect from its midgap donor level to the Γ, L and X conduction band minima. Furthermore, the broad band, clearly observed in the photocurrent spectrum taken before photoquenching, is very characteristic for the EL2 defect as measured in bulk GaAs [19]. This phenomenon is attributed to the A_1->T_2 intra-EL2 transition which can be followed by subsequent auto-ionization process with a release of electron into conduction band. The unique fingerprint of the EL2 defect, the photoquenching phenomenon, is widely accepted to be due to the light-induced metastable transition of the As_{Ga} defect into its nearest interstitial position, resulting in the formation of the As_i-V_{Ga} complex. We suggest that the broad band observed before illumination arises from the isolated defects which do not experience local strain of electrical fields and therefore can be quenched more efficiently. Moreover, we observed thermal recovery of photocurrent at 130 K which is very characteristic for the EL2 defect. All these fact demonstrate a direct experimental evidence for the existence of EL2-like defects and their importance for understanding of the optical and electrical properties of annealed LT GaAs.

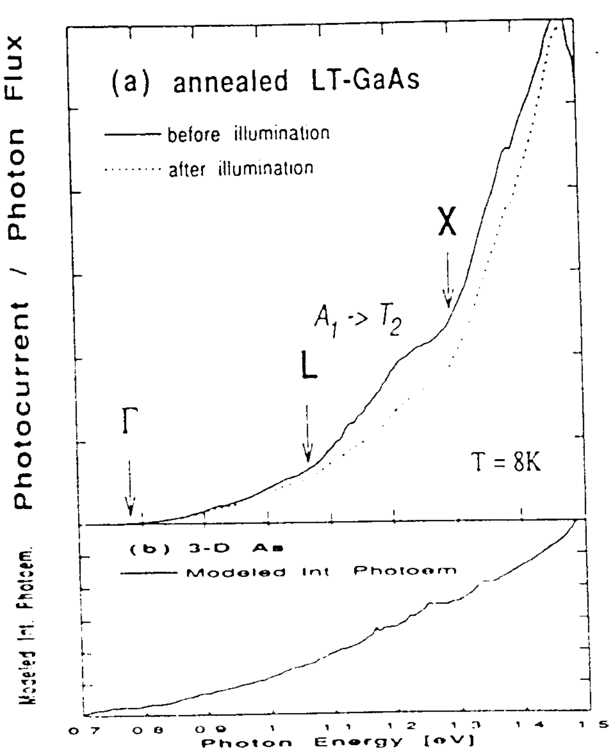

Fig.1: (a) Photocurrent spectra of a p-LT GaAs-n photodiode before and after photoquenching; partial photoquenching and three characteristic onsets typical for EL2 are clearly visible. (b) Modeled internal photoemission spectrum of As precipitates in the limit of small clusters, using the As band structure derived from ab-initio density functional calculations.

We have examined very closely the possibility if the photocurrent spectra can be explained based on the buried Schottky model. In order to determine the expected wavelength-dependence of the photocurrrent from As clusters, we modeled the internal photoemission process in the limit of small clusters. From local density ab-initio calculations using the LMTO method, we calculated the bulk As band structure. For the analysis of the internal photoemission process all direct transitions with sufficient energy in the final state to overcome the Schottky barrier height of 0.7 eV were integrated over the energy range of interest. The calculated spectrum, presented in Fig. 1b, is smooth with small features at energies between 1.15 to 1.35 eV, none of which were observed experimentally. Thus, this result does not show any of the characteristic features of the experimentally observed photoresponse. Therefore, our calculations support the conclusion that the spectral dependence of the photocurrent is not dominated by internal photoemission at buried Schottky contacts.

Summarizing, we found clear evidence that the "internal photoemission" spectrum is actually due to photoexcitation from As_{Ga}-related point defects, showing partial photoquenching typical for EL2 and the three onset energies at 0.76, 1.08 and 1.3 eV well known from the photo-ionization of the EL2 midgap donor to the three minima of the GaAs conduction band. On the other side, the calculated internal photoemission spectrum from small As clusters does not show the features observed here, and is not expected to exhibit any photoquenching effect.

3.1.2. Magnetic Circular Dichroism of as-grown and annealed LT GaAs

Photocurrent spectroscopy above clearly indicates the substantial presence of As_{Ga} defects in annealed LT GaAs. However, see e.g. [6,10,12], after annealing, most spectroscopic methods fail to determine the concentration of residual point defects, which was the main justification for the

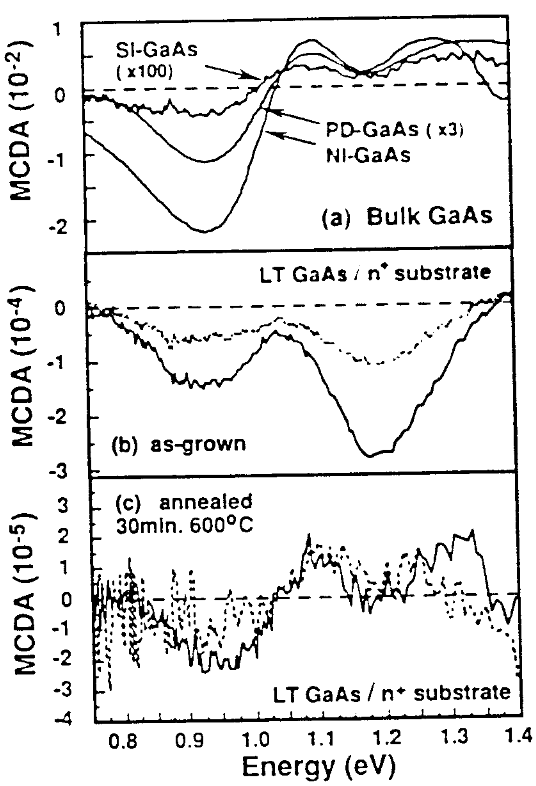

Fig. 2: Magnetic circular dichroism spectra of different GaAs samples, which show the unique one derivative and one bell-shaped bands due to $As_{Ga}{}^{+}$-related defects: (a) bulk semi-insulating GaAs; (b) as-grown (T_g = 210°C) LT-GaAs; and (c) annealed (T_a = 600°C) LT GaAs. The solid line represents the spectra from the samples cooled in the dark, the dashed line represents the spectra after the samples were quenched with a white light source. The spectra were taken at B = 2T and T = 1.8 K.

buried Schottky barrier model. In order to find out whether the As_{Ga} defects are responsible for the semi-insulating properties of the annealed LT GaAs, their concentrations have to be determined. We employed magnetic circular dichroism (MCD) as a more sensitive method for the determination of point defect concentrations in thin films [20], as described in detail in our previous proposal. Using n^+ substrates with very low concentration of EL2 we succeeded for the first time to directly determine the concentration of paramagnetic As_{Ga} defects in annealed LT GaAs. It was found that, typically for a LT GaAs grown at 200 °C and annealed for 30 min., the $[As_{Ga}{}^0]$ is about $10^{18}cm^{-3}$ and that of $[As_{Ga}{}^+]$ about $10^{17}cm^{-3}$ (Fig. 2) [21].

The simultaneous presence of both neutral $As_{Ga}{}^0$ defects and paramagnetic $As_{Ga}{}^+$ defects found above for the first time is a strong evidence that the Fermi level in annealed LT GaAs is pinned at the first donor level of As_{Ga} defects. We further systematically study two series of samples: LT GaAs grown at different temperatures, and LT GaAs annealed at different temperatures [22].

For LT GaAs grown at 200 °C and then isochronically annealed, the $[As_{Ga}{}^0]$ and $[As_{Ga}{}^+]$ in the materials are plotted in Fig. 3a as a function of annealing temperature. Although both $[As_{Ga}{}^0]$ and $[As_{Ga}{}^+]$ decrease upon annealing, we find that the defect concentration is high, and $[As_{Ga}{}^0] > [As_{Ga}{}^+]$ holds for all the samples investigated. Transmission electron microscopy (TEM) of the same samples show that the onset of precipitate formation is at ~400 °C [23]. Significant decrease in both $[As_{Ga}{}^0]$ and $[As_{Ga}{}^+]$ also starts at similar temperatures. However, it is clear that $[As_{Ga}{}^0] > [As_{Ga}{}^+]$ is maintained during the formation of the precipitates. Fig. 3a actually reveals the history of the formation of As precipitates. A study of the history indicates that the annealing dynamics is a process of forming As precipitates in the GaAs matrix in which the Fermi level is close to midgap. A near-flat-band condition is thus maintained in the process of precipitation with little charge transfer expected between the GaAs matrix and the As precipitates. Clearly, what really dominates the compensation mechanism of LT GaAs during the whole annealing sequence is the As_{Ga} defects.

An activation energy of about 1.4 eV is observed in Fig. 3a for the disappearance of both

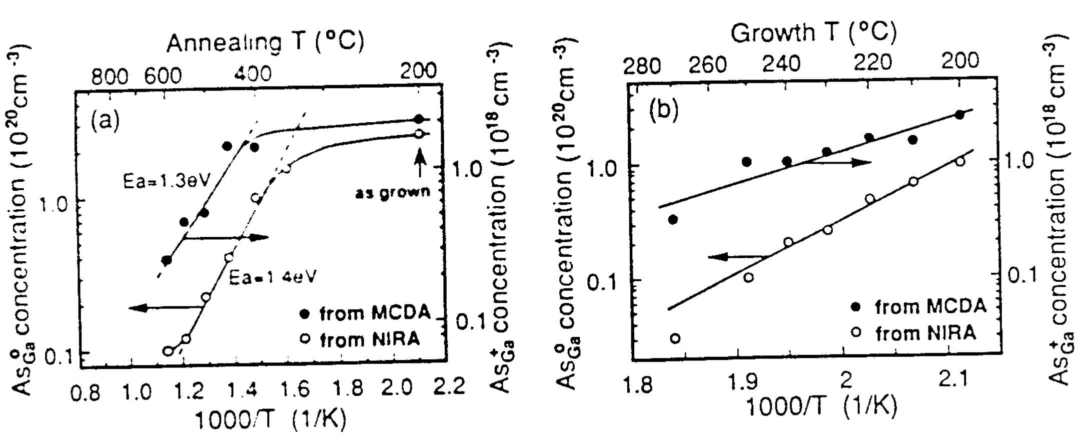

Fig. 3: Concentration of $As_{Ga}{}^0$ and $As_{Ga}{}^+$ determined by near-infrared absorption and magnetic circular dichroism, respectively, for (a) LT GaAs grown at 200°C and isochronally annealed; and (b) LT GaAs grown at different temperatures.

$As_{Ga}{}^{o}$ and $As_{Ga}{}^{+}$ defects. The activation energy is much lower than the As_{Ga}-related defects in bulk liquid-encapsulated Czochralski (LEC) grown GaAs. Such a small activation energy is consistent, however, with a process of Ga vacancy-assisted diffusion of the As_{Ga} defects to As precipitates [24]. Since Ga vacancy is a triple acceptor, it is very likely to be the dominant acceptor in LT GaAs. Our results thus measure also the concentration of Ga vacancies, which is about one third of that of $As_{Ga}{}^{+}$ defects.

For LT GaAs grown at different temperatures, it has been observed that the resistivity of as-grown LT GaAs increases with growth temperature, and best semi-insulating properties are achieved at ~400 ^{o}C [25]. Fig. 3b shows the As_{Ga}-defect concentration as a function of growth temperature. Both charge states of the As_{Ga} defects are present in a high concentration. They decrease as the growth temperature increases, with $[As_{Ga}{}^{o}]$ dropping faster than $[As_{Ga}{}^{+}]$. However, for all the growth temperatures studied, substantial As_{Ga} defects are detected with $[As_{Ga}{}^{o}] > [As_{Ga}{}^{+}]$. Extrapolating the results in Fig. 3b to the growth temperature of 400 ^{o}C, we obtain $[As_{Ga}{}^{o}] \sim 1\times10^{17}/cm^3$, and $[As_{Ga}{}^{+}] \sim 5\times10^{16}/cm^3$. In as-grown LT GaAs As precipitates have never been observed. The semi-insulating, as-grown material is thus a unique case to test the validity of the defect model. The mechanism responsible for the semi-insulating properties of annealed LT GaAs and the LT GaAs grown at higher temperatures may be very relevant, or even the same. Results in Fig. 3b indicate that As_{Ga} defects dominate the electrical properties of the as-grown LT GaAs. At the lowest growth temperature, high concentrations of As_{Ga} defects in two charge states lead to strong hopping conduction in the material. Note that the existence of $As_{Ga}{}^{+}$ defects is a necessary condition for the bound carriers to hop between the defects. With increasing growth temperature, due to the decrease of As_{Ga} defects, the hopping is significantly suppressed. The defect concentration, however, is still high enough to compensate the material, pin the Fermi energy close to midgap, and render the material highly resistive. Hopping conduction is negligible at the low defect concentration expected above for the material grown at ~400 ^{o}C. The concentration, however, is higher than normal bulk LEC GaAs which is undoped and semi-insulating. Obviously, the semi-insulating properties can be well accounted for by the As_{Ga} defects, although As precipitates do not even exist in the as-grown material.

Summarizing, we find that As_{Ga} defects in undoped, both as-grown and annealed LT GaAs at different temperatures are abundant, with the concentration of $As_{Ga}{}^{o}$ higher than that of $As_{Ga}{}^{+}$ defects. In contrast, As precipitates are not observed in the as-grown material. In the annealed material the precipitates are formed in a GaAs matrix in which the Fermi energy is close to midgap. A near-flat-band condition is thus maintained in the process of precipitation with little charge transfer expected between the GaAs matrix and the precipitates. The semi-insulating properties of the undoped LT GaAs thus are not caused by precipitates, while As_{Ga} defects can well account for the pinning of the Fermi level close to midgap, and hence the semi-insulating properties of the material.

An interesting question that is still unresolved pertains to the nature of the As_{Ga} -related defects in LT GaAs. These defects show several features that are distinctly different from As_{Ga} in as-grown GaAs: they are only partially photo-quenchable, do not show a zero-phonon line in optical absorption, show a different MCD-spectrum, and Hall effect measurements show a smaller activation energy near 0.65eV than typical for the midgap donor level of As_{Ga} [26]. It remains to be seen whether these differences are caused by the strain fields or the presence of other defects in LT GaAs or are indicative for a different atomic structure of the As_{Ga} - related defects in this material.

3.1.3. *Nuclear Magnetic Resonance of ^{75}As in GaAs*

In order to find a new method to study the behavior of *all* excess As in LT GaAs, we started in a collaborative project with Prof. J. Reimer from the Department of Chemical Engineering the study of ^{75}As NMR in GaAs, as we had suggested in the previous proposal. Compared to EPR, this method has the advantage that it is sensitive for all paramagnetic ^{75}As (100% abundance), independent of its charge state. The disadvantage is obviously that the response from lattice ^{75}As has to be distinguished from the response from ^{75}As at defect sites. It turned out that using a spin-echo technique ("nutation spectroscopy") [27] it is possible to obtain characteristic responses from As in perfect sites and As in defective sites, as evidenced from the spectra of n-irradiated GaAs in Fig. 4a. Fig. 4b shows spectra of plastically deformed GaAs, compared with as-grown and annealed LT GaAs. It is obvious that the different As-related defect populations are reflected in different nuclear quadruple interactions (sharp peak), but a rigorous model will have to be developed to quantitatively understand these novel types of spectra.

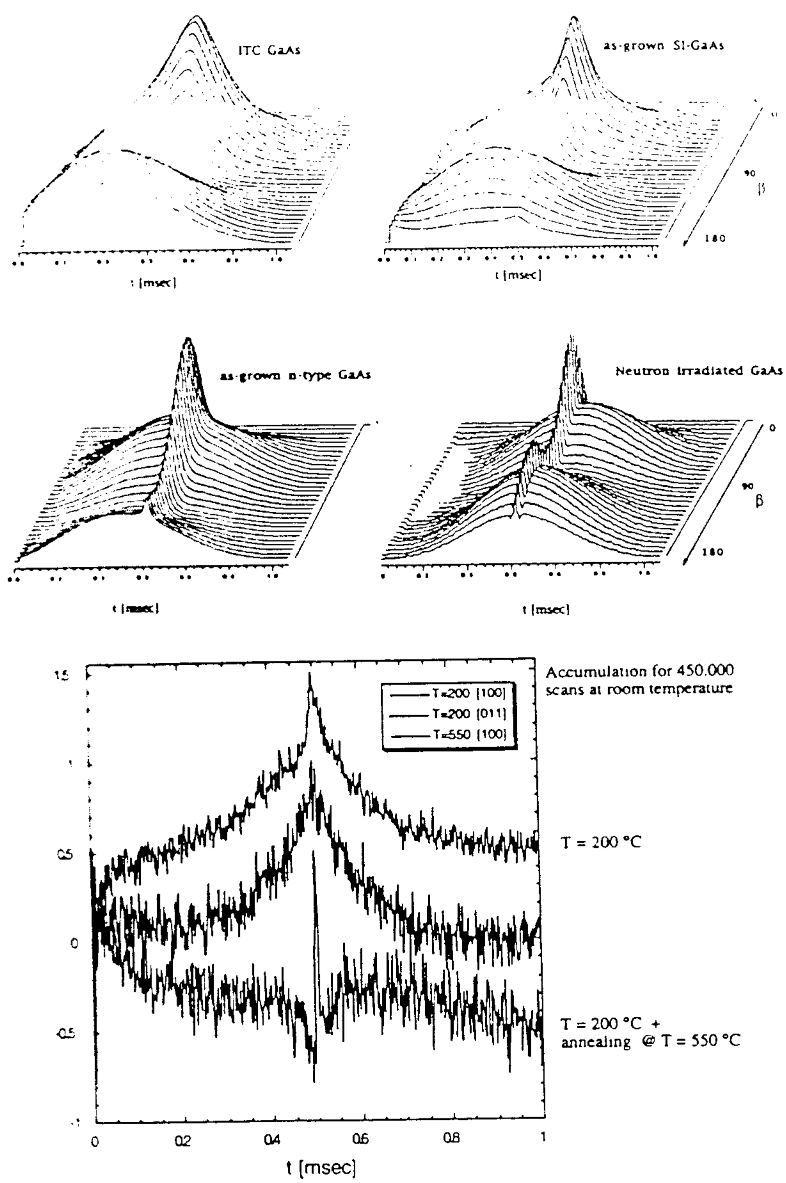

Fig. 4: a) NMR nutation spectra of LEC s.i. GaAs and n-type GaAs, annealed GaAs (ITC: after additional EL2-annealing by quenching from high temperature), and n-irradiated GaAs (10^{17}n/cm^2).

b) NMR nutation spectra of as-grown and annealed LT-GaAs, compared with the spectrum of dislocation-rich plastically deformed GaAs with 6×10^{16} As_{Ga}^{+} /cm^3; note the annealing-induced disappearance of the broad shoulders of LT-GaAs caused by dipolar broadening.

3.2. Low-temperature-grown InP

Whereas low-temperature grown GaAs is semi-insulating, low-temperature grown InP was found to be highly conductive [28]. This unexpected result stimulated us to study this material in detail, as we expected that similarly as in GaAs anion antisite defects are the dominant lattice defect. The electronic structure of the anion antisites in GaAs [8] and GaP [29] is relatively well known, both introducing near mid-gap deep levels. Our understanding of the electronic structure of anion antisites in InP (i.e. P_{In}) has been very poor. One of the main reasons for this has been the lack of experimental data due to the difficulty to introduce in significant concentrations the P_{In} antisites into bulk InP by conventional stoichiometric growth techniques.

However, InP grown by LT MBE under phosphorus overpressure was expected to contain P_{In} antisites in a very high concentration which could dominate the electrical and optical properties of this material, similarly to LT GaAs. Therefore, in collaboration with the group of Prof. C.W. Tu from UC San Diego we have undertaken systematic and detailed studies of the electronic and optical properties of LT InP grown by gas source MBE. In our studies we utilized advanced characterization techniques such as a variable-temperature and high pressure (up 1.5 GPa) Hall effect measurements, Deep Level Transient Spectroscopy (DLTS) on p^+-n diodes (both techniques applied for the first time to InP), Optically Detected Magnetic Resonance studies (ODMR), high-resolution Photoluminescence (PL) as well as ODMR- and PL-excitation spectroscopy.

3.2.1. Electrical Studies of LT InP

We found at growth temperatures (T_g) below 350°C a metallic-like electrical transport indicating that the electrons form a degenerate gas in the conduction band (CB). For samples grown at $T_g \leq 265$ °C the electron concentration saturated at 4 x 10^{18} cm^{-3}. The dramatic increase of the *n* with decreasing T_g suggested a growth-temperature-dependent incorporation of native donor-like defects [30].

Fig. 5 shows the pressure dependence of the free electron concentration in LT InP measured via the free carrier infrared absorption [30]. The pressure-induced disappearance of free carrier absorption indicated that there should be a deep donor level, resonant with the conduction band at p=0. We proposed that with increasing pressure the level moves down with respect to the CB minimum and captures free electrons. Based on these measurements, the energy of the donor level was estimated to be 0.11±0.02 eV above the bottom of the CB at ambient pressure.

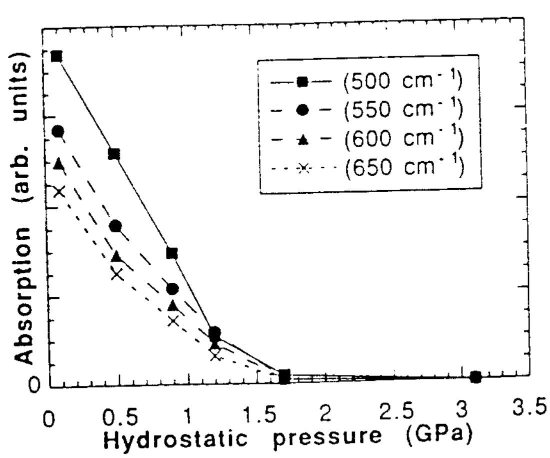

Fig. 5: Far-infrared optical absorption of LT InP grown at 200°C for different photon energies as a function of the hydrostatic pressure at T= 5 K.

The isothermal pressure dependances of the free electron concentration was studied directly at 77 K and 296 K with pressure-dependent Hall measurements [31], confirming the presence of a deep donor level resonant with the CB at *p*=0, which via autoionization process provides free

electrons. In order to characterize those effects more quantitatively as well as determine the thermal ionization energy E of the donor level and its pressure shift we made a detailed numerical analysis based on the charge neutrality equation. We were able to model the experimental $n(p)$ dependances assuming four fitting parameters (thermal energy $\varepsilon^{+/0}$ and its pressure derivative $d\varepsilon^{+/0}/dp$, shallow donor and acceptor concentrations, N_D and N_A, respectively) [31]. The thermal ionization energy of 120 - 140 meV thus derived agrees perfectly with the Fermi level position ($E_F = E_{CB}$ + (120 - 140) meV) derived from the upper saturation limit of the free electron concentration n=4x10^{18} cm^{-3} found for all the LT epilayers grown at T_g≤265°C and in other studies of phosphorus-rich LT InP [28,32]. A similar Fermi level pinning was observed in the surface layer of bulk InP annealed under P overpressure [33]. This finding implies that the higher the deviation from InP stoichiometry, the higher the incorporation of the defects responsible for the increase of the electron concentration. Nevertheless, the Fermi energy cannot be higher than the energy position of the deep level at E_{CB}+(0.12-0.14) eV which determines the saturation limit n=4x10^{18} cm^{-3}. This finding has very important technological consequences, as the location of the donor level and its auto-ionization preclude as-grown nonstoichiometric P-rich InP from being semi-insulating material, in disagreement with previous claims. Another important finding is the large pressure derivative of the level, 105 meV/GPa, which can be compared with the pressure shift of InP band gap energy of 84 meV/GPa. This strong pressure dependence is characteristic for states formed by deep defects like transition metal ions reflecting pinning of their energy to the pressure-independent neutrality level. The large pressure derivative of the (0/+) donor level reveals that the wave function of the donor defect is indeed highly localized.

Although the E_{CB} + 0.12 eV defect level controls the electrical properties of LT InP, there is still an open question as to whether there are other levels associated with the same defect. Our Hall effect measurements showed that a defect level with thermal ionization energy of 0.22 eV exists in this material [30]. To verify if this defect level can be detected using other experimental techniques we performed DLTS measurements on uniquely manufactured p$^+$n junctions (undoped n-type LT InP epilayers grown on p$^+$ InP substrate). The DLTS results revealed the presence of two electron traps in LT InP with activation energies of 0.25 eV and 0.53 eV. No other levels shallower than 0.25 eV were detected. Most likely, the thermal ionization energy E_T= 220 meV (Hall effect) and activation energy of the emission process E_e=250 meV (DLTS) are due to the same defect. The optical studies described below confirmed that the second ionization stage of the isolated phosphorus antisite defect, $P_{In}^{+/++}$, is located in the upper half of the band gap at energy $E < E_{CB}$ - (0.3±0.1) eV. Therefore we assign the E_{CB}-220 meV level to the $P_{In}^{+/++}$ level. Since no other energetically shallower deep levels have been found in the band gap neither using Hall nor DLTS measurements, the most natural identification of the deep level resonant with the conduction band at E_{CB}+0.12 eV is that this is indeed the first ionization stage $P_{In}^{0/+}$ of the phosphorus antisite double donor.

3.2.2. *Optical studies of LT InP*

In an attempt to determine the optical ionization energy of the second ionization stage of the phosphorus antisite defect, $P_{In}^{+/++}$, we applied ODMR excitation spectroscopy, a powerful technique which gives the correlation between the identification of the deep defects and their energetic position [34,35]. In these experiments the individual line and thus the corresponding defect were monitored while the optical excitation photon energy was varied by a tunable laser. The onset of the band-to-defect level transition gives an information on the energy level position of the

defect under study.

In Fig. 6 we show the ODMR spectrum and an excitation spectrum obtained from the Be-doped sample grown at 310°C. Similar spectra were obtained for the ODMR singlet (Be complex) and doublet (P_{In} antisite). Besides the excitation of the InP across the band gap, there are two other resonant transitions which enhance the ODMR signals related to the P_{In} antisite and the Be complex at energies near 1.25 eV and 1.34 eV, respectively. These two transitions correspond to the excitation between the band edge and the defect levels involved in the ODMR, as shown in Fig. 6. This is consistent with the defect energy of E_{CB}-0.23 eV for the P_{In} $^{+/++}$ level obtained from electrical measurements. The decrease in the ODMR signal at 1.39 eV is most likely to be due to the transition from the Be-complex at E_{VB}+0.03 eV to the CB. We would like to point out that there is no indication from the excitation spectra that the (0/+) level of the phosphorus antisite is within the band gap. This is consistent with the fact that we have not detected in the electrical studies such a $P_{In}{}^{0/+}$ level of the antisite below the CB edge. This result is futher supported by the observed correlation between the free-electron concentration and MCD intensity of the $P_{In}{}^{+}$ antisite in LT InP as a function of growth temperature. [36]

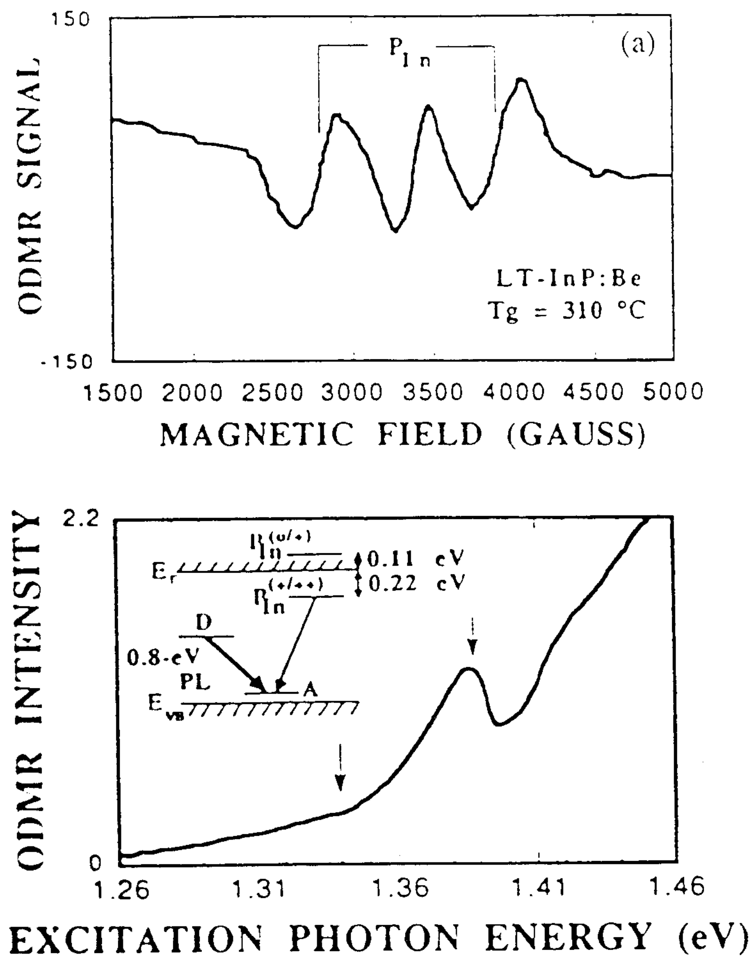

Fig. 6: (a) ODMR spectrum from a Be-doped LT InP, and (b) ODMR excitation spectrum and suggested level scheme of P_{In} in InP.

Summarizing, we found direct experimental evidence that the electronic properties of LT InP are determined by the presence of a deep localized donor defect which via auto-ionization provides the electrons to the conduction band and therefore is responsible for the n-type character of the P-rich InP. We concluded that this level is the first ionization stage of the antisite defect $P_{In}{}^{0/+}$. We have determined its energetic position and shown that this donor defect is highly localized in real space. We have obtained consistent results from Hall effect, DLTS and ODMR-excitation spectroscopy which led to the determination of the energetic position of the second ionization stage of the phosphorus antisite, $P_{In}{}^{+/++}$. So we succeeded ten years after the determination of the two energy levels of the As_{Ga} antisite defect in GaAs to determine the corresponding levels of the P antisite in InP. Although it appears to be impossible to obtain semi-insulating LT InP, this unique material might find interesting applications. These could range from intermediate contact layers to strain sensors, based on the strong strain dependence of carrier concentration in LT InP.

3.3. Superconductivity in In-doped GaAs

In the course of the study of LT GaAs with magnetic resonance, a completely unexpected effect was discovered: evidence for superconductivity in GaAs [37]. This effect was detected through ultra-sensitive microwave absorption measurements possible with an EPR spectrometer. Below a transition temperature of about 10 K, several effects typical for microwave absorption by superconductors in such a set-up [38] were found: strong absorption near zero field, hysteresis typical for trapped flux, and characteristic instabilities detectable as increased noise near the transition temperature. The effect was reproduced at several laboratories, see e.g. [39].

These effects were first found in samples containing LT GaAs layers, but it later turned out to be due to In diffused into the GaAs from the wafer backside during heat treatment at temperatures above 400°C [40]. TEM analysis of the samples showed In-rich regions several 100μm deep in the GaAs wafer which were heavily distorted by dense dislocation networks. The superconductive phase has a transition temperature far above the critical temperature of crystalline In, but close to the transition temperature of amorphous In, which is usually unstable at temperatures above 100 K. Thus it appears that within the GaAs crystal a heavily distorted, possibly amorphous phase of In can be stabilized; heat treatment above 130°C can destroy this phase, but heating above 400°C followed by rapid cooldown re-creates this phase.

At present it appears that these unconnected pockets of superconductive phase are only of fundamental interest, e.g. for the study of the stabilization of an amorphous phase inside a crystal, or for the study of small superconductive clusters. In addition, the surprising result of long-range diffusion of In for distances of the order of 100μm during about one hour at temperatures near 500°C is of interest, too, especially for MBE-growers using In bonding of the wafer for better thermal contact to the substrate holder. It remains to be seen whether these results will be of relevance for a device application.

4. Future Work

For the continuation of the research described in this report, a proposal has been submitted to AFOSR with the title "Non-Stoichiometric Layers of III/V Semiconductors". This proposal suggests a 3-dimensional approach for further the understanding, developing, and device application of the non-stoichiometric Semiconductors. Based on a better understanding of low-temperature-grown semiconductors due to our previous research, we plan develop optimized layers of non-stoichiometric semiconductors and to facilitate in their implementation in device applications. Since As antisite defects have been found to control the special properties of LT GaAs, and the As precipitates not taking part in any relevant change of materials properties, the precipitates might even be detrimental, e.g. for carrier mobility. It should be possible to design As-rich GaAs with the proper amount of excess As, avoiding the formation of potentially detrimental As precipitates. We propose two approaches towards this goal: (i) varying the substrate temperature and the As/Ga flux ratio to introduce well-controlled amounts of excess As into LT GaAs; (ii) Using different annealing treatments to control the amount of excess As that precipitates

during the thermal treatment. We plan to continue our basic study on the new materials and to use the advanced materials to fabricate and test device. In addition, we plan to expand our study to other III/V compounds and alloys which may have new and better device properties. We also plan to use As implantation to achieve As-rich GaAs as an alternative to low-temperature MBE growth.

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